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Screen printed conductive CuS-poly(acrylic acid) composite coatings

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Abstract

Copper sulfide (CuS) powder precipitated from two different chemical baths (citrate and triethanolamine baths) was dispersed in a poly(acrylic acid) aqueous solution and the resulting mixtures were screen-printed over glass slides. Compared to the coatings of the same composite materials obtained by casting, the screen-printed coatings show better homogeneity and an improved thermal stability (up to 300°C). Sheet resistances of 50 Ω/□ were typical in 20 μm thick coatings and these values remained stable even after baking in nitrogen or vacuum at 200–300°C. The X-ray diffraction pattern indicates degradation of CuS to Cu_{1.8}S and Cu_{1.96}S, particularly in air-baked samples at 250–300°C. The XRD, TGA and R_□ results show CuS(Cit)-PAA samples as superior conductive coatings. © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Copper sulfide thin films and coatings have been widely studied and used for solar energy applications [1–3]. We have reported earlier that CuS thin films can be easily grown on glass and acrylic substrates by a chemical bath deposition technique to

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serve as spectrally selective surfaces in solar control glazings [4–8]. During the deposition of thin films by this technique, fine CuS powder is also precipitated in the chemical bath, which has been used to form electrically conductive CuS-poly(acrylic acid) composite coatings [9]. Such coatings are prepared by dispersing the CuS powder (precipitated from the triethanolamine bath) in a poly(acrylic acid) (PAA) aqueous solution and casting the mixture onto glass slides. The CuS–PAA composite coatings are formed upon evaporation of the solvent. Measurement of sheet resistance (R_{\square}) indicates a percolation threshold of electrical conduction at a weight percent of about 40% of CuS in the composite, at which the composite undergoes a transition from an insulator ($R_{\square} \sim 10^{13} \Omega$) to a conductive state ($R_{\square} \sim 10^2 \Omega$). These CuS–PAA composite coatings prepared by the casting method described above possess electrical conductivities which are stable even after baking in air at temperatures upto 250°C [9]. Baking at higher temperatures between 250°C and 300°C results in an increase of sheet resistance ascribed to a decomposition mechanism: the conversion of CuS to $\text{Cu}_{1.8}\text{S}$ and the thermal expansion of PAA in the composite.

In the present work, we report an alternative method to prepare the CuS–PAA composite coatings by the screen printing technique. Compared with a coating obtained by casting which dries in about 24 h, a freshly prepared screen printed coating dries faster (in a few minutes at about 50°C), leaving a thinner and more uniform film. However, a screen-printed film of certain pigments is formed usually by mixing a flux material to fuse the pigments during annealing. Screen-printed films of CuS have been prepared using copper nitrate as flux to fuse CuS pigments to enable the binding of the CuS powder [10]. But the decomposition of copper nitrate at temperatures around 200°C has been found to deteriorate the thermal stability of these coatings. In the CuS–PAA composite, PAA substituted copper nitrate in its role as a flux. Poly(acrylic acid) acts as a binder for CuS pigments: the polymers functional groups (–COOH) adsorb to the surface of the CuS pigments to form a heterogeneous composite coating. The quality of screen-printed CuS–PAA coatings is better than the coatings prepared by casting [9] and they possess better thermal stability than the coatings obtained by the screen printed and sintering process using $\text{Cu}(\text{NO}_3)_2$ as a flux [10].

2. Experimental details

CuS powder was precipitated at room temperature (25°C) from two different chemical baths: (a) The TEA bath was prepared with 5 ml of 0.5 M CuCl_2 , 4 ml of 3.75 M triethanolamine (TEA), 4 ml of 15 M NH_4OH , 5 ml of 1 M NaOH, 3 ml of 1 M thiurea, and 29 ml of deionized water to take the final volume to 50 ml [4–6]; (b) The citrate bath contained 2 ml of 0.5 M CuCl_2 , 12 ml of 0.5 M sodium citrate, 35 ml of deionized water and 1 ml of 1 M thioacetamide [7]. To obtain sufficient quantities of the precipitates, 400 ml of each solution was usually prepared. At 15 h after the constitution of the solutions, the precipitates were filtered, washed in deionized water, and dried in an air oven at 50°C for about 12 h. The precipitates are

labeled as CuS(TEA) in the case of CuS powder precipitated from the TEA bath and CuS(Cit) when the precipitate has been obtained from the citrate bath.

The CuS powder obtained as above was dispersed in propylene glycol and then mixed with poly(acrylic acid) (PAA) aqueous solution (supplied from Aldrich with average molecular weight of PAA as 90 000) containing 25 wt% of PAA solid. The CuS weight percent in the composite (that is, the weight of CuS divided by the sum of the CuS weight and the PAA solid weight) was chosen as about 68% for two reasons: first it must be greater than the percolation threshold (40%), otherwise the composite would not be conductive; second it gave a suitable viscosity of the mixture to enable the formation of a screen printed coating. The CuS–PAA mixture was screen printed through a polyester screen of 120T mesh on clean microscope glass slides of 75 mm × 25 mm × 1 mm and dried at 50°C in air. The typical thickness of the dried coatings is about 10–20 μm, which is much thinner than the cast films (about 50 μm) of the same material [9].

A pair of silver-print electrodes (5 mm length at 5 mm separation) were painted on the CuS–PAA coatings to enable the sheet resistance measurement. X-ray diffraction (XRD) patterns of the films were obtained with a Siemens D-500 system. Thermal analysis was carried out using a TA Instrument TGA 951 unit.

3. Results and discussion

3.1. Electrical properties of CuS–PAA coatings

CuS screen printed films prepared with $\text{Cu}(\text{NO}_3)_2$ as flux were electrically stable upto about 200°C [10]. The rapid decrease in current with temperature above 200°C was attributed to the decomposition of CuS and $\text{Cu}(\text{NO}_3)_2$ and its conversion to various sulfates. On the other hand, CuS–PAA casting films showed a better thermal stability in air up to 250°C [9]. In order to see the effects of annealing atmosphere, the screen printed CuS–PAA composite coatings have been heated in the present case for 1 h in air, in nitrogen and in vacuum (100 mTorr, with nitrogen leakage to minimize the presence of oxygen). The sheet resistance of the heat-treated samples were measured at room temperature as a function of the annealing temperature.

Fig. 1 shows the sheet resistance (R_{\square}) of screen printed coatings of CuS(TEA)–PAA composite material annealed in air and in nitrogen. As the annealing temperature increased from 25°C to 200°C the sheet resistance of the coatings decreased due to the crystallization of the as prepared CuS powder [4,10]. Beyond 200°C, the effect of the annealing atmosphere is evident: the sheet resistance of the CuS(TEA)–PAA coatings annealed in air increases as the annealing temperature increases above 200°C; and under nitrogen atmosphere this increase occurs above 250°C.

Similar electrical properties of the coatings in air and in nitrogen annealed samples are also observed for CuS(Cit)–PAA screen printed coatings in the same figure, with the difference that the extent of increase in R_{\square} as a function of temperature above 200°C is much less than in the CuS(TEA)–PAA sample. After annealing at 250–280°C for 1 h in nitrogen, R_{\square} is stable around 20–50 Ω. And even after heating in air at

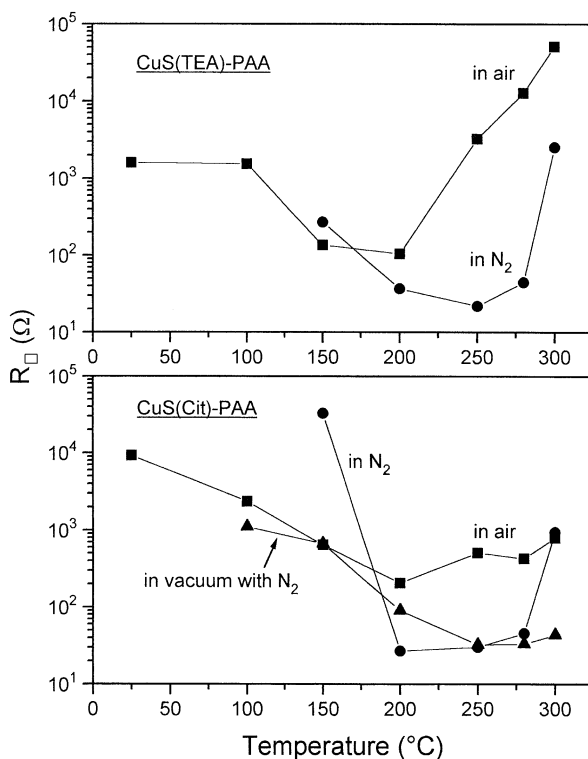


Fig. 1. Sheet resistances of CuS(TEA)-PAA and CuS(Cit)-PAA screen printed coatings as a function of annealing temperature and atmospheres.

300°C, the sheet resistance is rather low, about 1000 Ω. The copper sulfide precipitate obtained from the citrate bath appears to be thermally more stable than the CuS precipitate from the TEA bath.

In the vacuum annealing process (100 mTorr) the CuS(TEA)-PAA composite coatings were cracked and peeled off from the glass substrates at all annealing temperatures (from 100°C to 300°C). However, the CuS(Cit)-PAA films survived and showed a better thermal stability comparable with nitrogen annealed CuS(Cit)-PAA coatings. After annealing at 300°C for 1 h in that vacuum their R_{\square} is still approximately 50 Ω. That is to say that the CuS(Cit)-PAA coatings show a better adhesion on glass substrates in vacuum than the CuS(TEA)-PAA coatings.

3.2. X-ray diffraction patterns of CuS(Cit)-PAA coatings

Since the CuS(TEA)-PAA screen printed coatings show nearly the same XRD patterns as those of the CuS(Cit)-PAA samples, only XRD patterns of the latter are shown in the following figures: Fig. 2 for annealed in air; Fig. 3 for samples annealed in nitrogen and Fig. 4 for samples annealed in vacuum (100 mTorr).

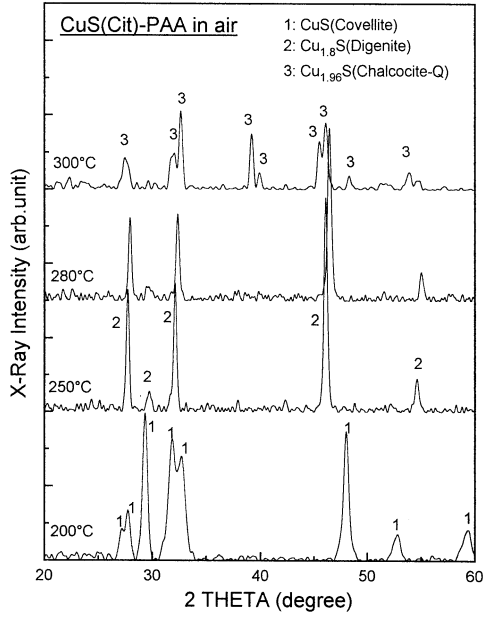


Fig. 2. X-ray diffraction patterns of CuS(Cit)-PAA screen printed coatings after annealed in air at different temperatures.

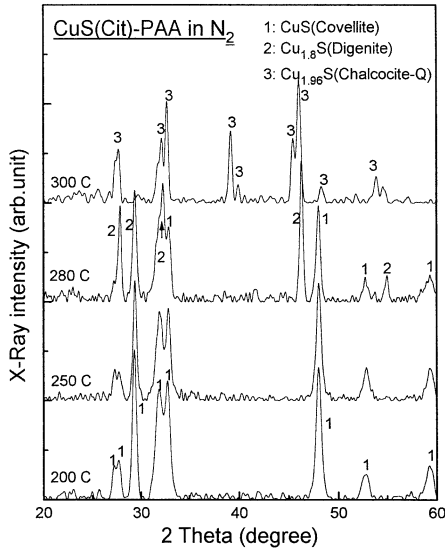


Fig. 3. X-ray diffraction patterns of CuS(Cit)-PAA screen printed coatings after annealed in nitrogen at different temperatures.

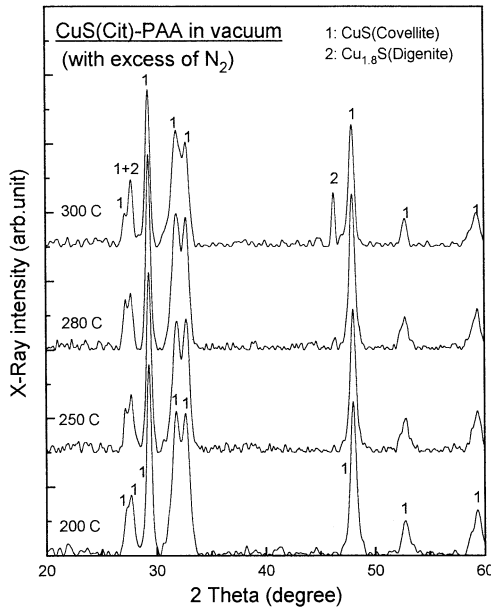
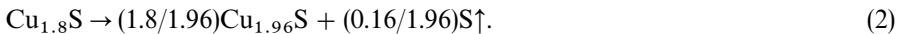


Fig. 4. X-ray diffraction patterns of CuS(Cit)-PAA screen printed coatings after annealing in vacuum (100 mTorr with nitrogen pressure) at different temperatures.

At temperatures $\leq 200^\circ\text{C}$ the screen-printed CuS-PAA composite coatings show only the crystallized CuS (covellite) phase, as in the case of the cast coatings of the same material [9]. At annealing temperatures above 200°C , the sublimation of sulfur in CuS-PAA samples is accompanied by two-phase transition processes: (1) from CuS (Covellite) to $\text{Cu}_{1.8}\text{S}$ (Digenite),



and (2) from $\text{Cu}_{1.8}\text{S}$ (Digenite) to $\text{Cu}_{1.96}\text{S}$ (Chalcocite-Q),



In the first process, each CuS molecule transforms to 0.11 molecule of $\text{Cu}_{1.8}\text{S}$ liberating 0.44 molecule of sulfur in the process, whereas in the second transition for each CuS molecule involved almost 0.49 molecule of sulfur is released.

From Figs. 2–4 it is clear that the temperatures at which these two transitions occur are a function of annealing atmosphere. The first transition is completed at 250°C in CuS-PAA screen-printed samples annealed in air (Fig. 2). However, the same transition sets in at a higher temperature (280°C , Fig. 3) if the annealing atmosphere is nitrogen. In vacuum with N_2 pressure (100 mTorr) this transition just starts at 300°C , (Fig. 4). When comparing the sheet resistance data in Fig. 1 with the XRD data in Figs. 2–4, it becomes evident that the phase transition from CuS (Covellite) to $\text{Cu}_{1.8}\text{S}$ (Digenite) causes the increases of the R_{\square} of the CuS-PAA screen printed samples

annealed in air (from 200 to 250°C), in nitrogen (from 250 to 280°C) and in vacuum (from 280 to 300°C).

The second transition ($\text{Cu}_{1.8}\text{S}$ to $\text{Cu}_{1.96}\text{S}$) observed in Figs. 2 and 3 is responsible for further increases of R_{\square} in samples annealed in air and in nitrogen from 280 to 300°C (Fig. 1). But in the samples of $\text{CuS}(\text{Cit})\text{-PAA}$ screen printed coatings annealed in vacuum with N_2 such a transition occurs only at the initial stage even at temperatures up to 300°C (Fig. 4), keeping a R_{\square} around 50 Ω (Fig. 1).

3.3. Thermogravimetric analysis

In order to study the thermal behavior of $\text{CuS}\text{-PAA}$ composite materials, thermogravimetric analyses (TGA) were carried out in air with a heating rate of 5°C/min for the three materials (Fig. 5): PAA, $\text{CuS}(\text{TEA})\text{-PAA}$ and $\text{CuS}(\text{Cit})\text{-PAA}$.

The PAA sample obtained from the aqueous solution used for TGA thermogram in Fig. 5 was preheated at 50°C for about 24 h. Therefore, the weight loss due to the free water (at temperatures < 100°C) was negligible. From 120°C to 170°C, with a maximum at 135°C, there is a weight loss due to release of lattice water in poly(acrylic acid). From about 200°C to around 280°C with a maximum at 245°C the weight loss in the PAA sample is attributed to the anhydride formation. Above 300°C the polymer chains start to decompose.

The TGA thermogram of $\text{CuS}(\text{TEA})\text{-PAA}$ composite (with a CuS weight percent equal to 4%) in Fig. 5 shows four maximum derivative peaks: the first one at about 138°C due to the release of lattice water incorporated in PAA and the last one at 306°C due to CuS decomposition. In contrast to the PAA sample, which shows the second peak at 245°C, the $\text{CuS}(\text{TEA})\text{-PAA}$ composite sample shows two middle peaks: the second at 200°C and the third at 220°C. Fig. 5 also shows the TGA thermogram of $\text{CuS}(\text{Cit})\text{-PAA}$ sample (with the same of 4 wt% of CuS in the composite). Similar results were obtained in this case except that the third peak in the derivative is around 247°C (near to that of the PAA sample instead of at 220°C for the $\text{CuS}(\text{TEA})\text{-PAA}$ sample).

We consider that the assignment of the second peak at 200°C in the TGA derivatives is a bit ambiguous. For example, in porous PAA-alumina composites [11], it is suggested that the peak at 200°C can be attributed to the release of tightly bound water, and that the anhydride formation occurs at about 250°C. If we take this assumption for the $\text{CuS}\text{-PAA}$ composite samples, the second peak in the derivatives of TGA (around 200°C in Fig. 5) should be attributed to the bound water, and the third peaks to the anhydride formation (T_{anh}). However, it was observed in $\text{Bi}_2\text{S}_3\text{-PAA}$ composites that such T_{anh} can also occur at temperatures about 200°C [12]. Therefore, we cannot discard at this moment the possibility that the 200°C peaks result from anhydride formation as well. Detailed thermal analysis (TGA and DSC) is in progress on metal chalcogenide- poly(acrylic acid) composites to analyze the binding mechanisms between the carboxylic groups of PAA and the metal sulfide surface.

The third peak in the derivatives of TGA of the $\text{CuS}\text{-PAA}$ composites should be assigned to an anhydride formation temperature (T_{anh}), noting that the anhydration occurred at about 247°C in $\text{CuS}(\text{Cit})\text{-PAA}$ material (just as the PAA sample),

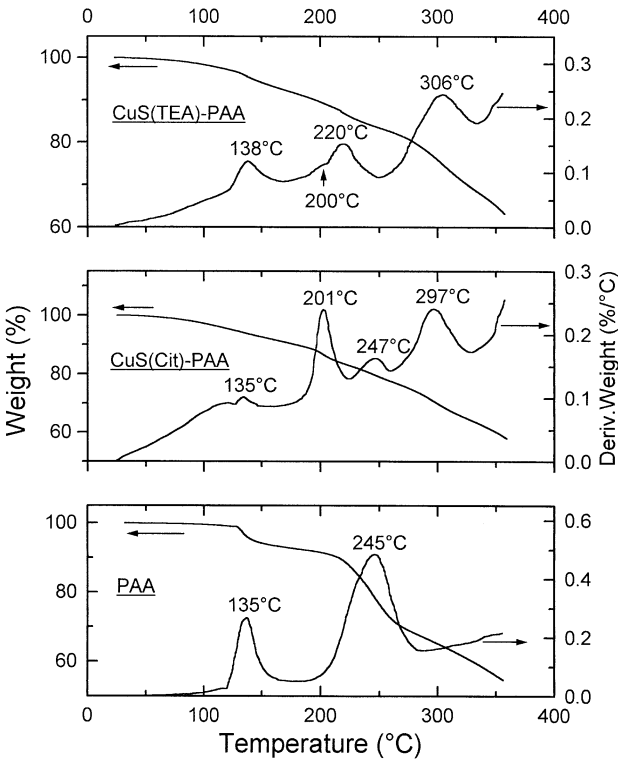


Fig. 5. TGA thermograms of CuS(TEA)-PAA, CuS(Cit)-PAA and PAA and corresponding relative TGA rate curves in air with a heating rate of 5°C/min.

whereas, the same process started at around 220°C in CuS(TEA)-PAA composite. Since the adhesion between the PAA and the inorganic powder is due to the adsorption of -COOH groups of PAA on the powder surface, the anhydride formation of -COOH would lead to the decomposition of the composites. Hence, it is expected that the higher the T_{anh} , the more stable the composite would be.

As observed in the same TGA thermograms, the compound CuS in the CuS-PAA composites started to decompose in air at temperatures above 280°C due to the sublimation of sulfur. If we annealed samples in an inert atmosphere this sublimation should be delayed. However, the same TGA results were obtained for the two CuS-PAA composite materials recorded under nitrogen flow during the heating. That is to say that since the thermobalance is an open system, a trace of oxygen is sufficient to oxidize CuS.

4. Conclusion

We have shown in this paper that it is possible to prepare a uniform and thermally stable coating of copper sulfide- poly(acrylic acid) composite by screen printing

technique. The CuS precipitate from the Citrate bath gives better thermal stability for the composite than the CuS powder precipitated from the TEA bath because of the higher anhydride formation temperature in CuS(Cit)–PAA composite. Sheet resistance of CuS–PAA coatings is about 50Ω at 280°C for samples annealed in nitrogen, and is maintained at this value even at 300°C when annealed in vacuum (100 mTorr with nitrogen pressure).

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